Dissertation.

The Action of Phenol

and

Chloride of Orthosulphobenzoic Acid

Dissertation

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by

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Contents.

Acknowledgment

This investigation was suggested by Professor Ira Remsen, and the work was carried on under his supervision. The author takes this opportunity to express his profound appreciation of the guidance and instruction received from Professor Remsen. He also desires to acknowledge his gratitude for instruction received from Professor Mayer, Dr. Remsen, Dr. Jones, Dr. Matthews, Professor Clark, and Dr. Whitlock.

Introduction.

[illegible] the action of phenol on what were then known as the solid and liquid chlorides of orthosulphobenzoic acid. When phenol was added to the mixed chlorides they passed into solution, but no reaction was observed to take place in the cold. On warming, the evolution of hydrochloric acid began at once, and the liquid assumed a dark, blood-red color which became more intense as the reaction proceeded. When poured into a hot solution of dilute sodium hydroxide, a crystalline product separated which proved to be the diphenyl ester of orthosulphobenzoic acid, $C_6H_4\begin{cases}SO_2Cl\\ CO_2C_6H_5\end{cases}$. When pure phenol alone was employed, the same products were formed as with a mixture of the chlorides. The liquid

[illegible] Chem. Jour. 17. 352.

chloride, when treated in the same way, showed the usual color reaction, and when the product was poured into dilute sodium hydroxide, a heavy, yellow oil settled to the bottom of the vessel and became crystalline after a time. On recrystallizing this from alcohol, two substances were isolated. One of these crystallized in needles and proved to be the dibenzyl ester of orthosulfobenzoic acid, and the other crystallized in clear, thin columns which melted at 95°-100°. The latter product was neither identified nor studied. The coloring matter was supposed to be fluorescein.

In the following year [illegible] repeated this work. They obtained the dibenzyl ester of orthosulfobenzoic acid without difficulty, but made no mention of finding the substance which melted at 95°-100°. They tried the effect of treating the reaction product

with dilute ammonia instead of [illegible]
hydroxide. In this case also, the reaction
is slowly, but satisfactorily when allowed to stand for
some time. This, when crystallized from alcohol,
yielded the diphenyl ester of orthosulphobenzoic
acid, and a new substance which was called
phenyl orthosulphamidobenzoate, and given the for-
mula $C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases}$. They described the crystals
as feathery-shaped, and gave the melting point
as 121°-122°. They were not able to analyze
the substance that formed this amide with
ammonia, but suggested it to be the o chlo-
rosulphonchloride of phenyl benzoate, $C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases}$,
formed according to the following equation:

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + C_6H_5OH = C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + HCl.$$

This ester, they thought, reacted with ammonia
to form phenyl orthosulphaminobenzoate in the fol-
lowing manner:

$$C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + 2NH_3 = C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases} + NH_4Cl.$$

In an article by Stenhouse and Gist on the chloride of o.thiosulphobenzoic acid, they make the following statement with reference to this phenyl o.thiosulphamidobenzoate obtained by Remsen and Hitchcock.

"On the contrary, in spite of the most careful experiments, we have in vain attempted to secure the phenyl ester of o.thiosulphamidbenzoic acid. According to our experiments, the ester does not seem to be capable of existence. We did not obtain it either by treating the reaction product of phenol and the chloride with aqueous ammonia, or by bringing together the pure phenyl ester chloride with ammonia water".

The [illegible] statement, [illegible] Remsen suggested the advisability of repeating the work of Hitchcock and of making a careful investigation of Phenyl o.thiosulphamidbenzoate and o.thiosulphonechloride of phenyl benzoate. The

results of the investigation are [illegible] in this paper.

Preparation of the Chlorides of Cacodylmethylarsine [illegible]

The method of preparation given by Dehn[1] was followed in most particulars. To obtain the best yield of the unsymmetrical chloride, the heating of time given for heating the mixture of neutral potassium arsenate, - four hours, was not found sufficient. It is better to continue the heating for eight or ten hours. The temperature must not be allowed to rise above 125°, as [illegible] ethyl chloride begins to be formed at that temperature. Great care must be observed in the distillation of the chlorides from benzine, as they may easily become dark colored. This is especially true in the case of the unsymmetrical

[1] Inaugural Dissertation, Johns Hopkins University 1902.

chloride. The benefit of the [illegible] be experienced if the following method is adopted:

A small quantity of purified lignoin is heated with the chloride on a water-bath to a temperature within one or two degrees of its melting point. The undissolved chloride is allowed to settle, and the clear solution is decanted into another beaker. This is now placed in a bath of ice-water and the solution is vigorously stirred to induce the formation of a crystal meal. The crystals are filtered off with suction, and dried on a porous plate. The process is repeated as often as necessary, using the same portion of solvent again and again. The product is snow-white and perfectly pure. When the solvent is heated above the melting point of the [illegible], on cooling, and settles to the bottom of the beaker before crystallization begins, and contaminates the crystals.

which afterward separate out. This method is a little tedious, but it has the merit of requiring only a small quantity of solvent and of giving a pure product.

Confirmation of the work of Remsen and McKee.

2½ grams of symmetrical chloride were heated with 2 grams (two molecules) of phenol in a test-tube for five hours at 140° 145°. The reaction proceeded very slowly and was accompanied by the formation of a red coloring matter, phenol [illegible]. The reaction products, [illegible], were poured into a small mortar containing ordinary dilute ammonia, and ground with a pestle. The mass formed a thick, [illegible] liquid which required at least an hour, and frequently, in repetitions of this experiment, four to five hours to solidify. The [illegible]

product was finely triturated, washed, dried and dissolved in 30 cc. of 5% aqueous [illegible]. On cooling, the diphenyl ether of orthoamidobenzoic acid separated out in [illegible] which were collected off and the filtrate evaporated down to a volume of 6 cc. On standing, small, heavy transparent crystals formed which melted at 120° C. and after recrystallization, at 121° C. This product corresponds in [illegible] to the diphenyl orthoisoamidobenzoate described by Hemmelmayr and Wilbee.

The above experiment was carried in many ways, but the general [illegible] were always the same. The reaction products were allowed to cool, and then poured into cold, [illegible] ammonia and washed with cold water. The yield of [illegible] was [illegible] but when treated with warm [illegible] and washed with hot water, it was considerably increased

loc. cit.

Working under the most conditions, there was obtained from 5 grams of the symmetrical chloride 3 grams of diethenyl ether of orthocarbethoxyphenoic acid and 1 gram of phenyl orthocarbethoxyphenylhydroxylamine.

2½ grams of the unsymmetrical chloride were heated with 2 grams of phenol for three hours at 40°-45°. The reaction was more rapid than in the case of the symmetrical chloride, but in general, it appeared to proceed in the same way. The mass was poured into dilute ammonia and then treated exactly as above. The diethenyl ether was extracted out of the solution in alcohol. The filtrate from this was concentrated and allowed to stand. None of the phenyl orthocarbethoxyphenylhydroxylamine was obtained. When the solution was brought almost to dryness, a small quantity of oil was obtained which had a strong odor of phenol.

phenyl orthosulfaminebenzoate by this process.

The substance obtained from the asymmetrical chloride gave the following analytical results:

I. 0.2973 gram gave 0.6098 gram CO_2 and 0.1095 gram H_2O.

II. 0.3455 " " " 0.0625 " "

III. 0.2028 " $BaSO_4$.

IV. [illegible] required 15 cc. standard sulfuric acid (1 cc. = 0.00256 gram N), less 2 cc. standard soda (1 cc. = 0.004125 gram N). Kjeldahl method.

	Calculated for $C_6H_4<^{COOC_6H_5}_{SO_2NH_2}$.	Found.	
C	56.12	55.90	[illegible]
H	3.74	4.01	4.16
N	5.24	5.08	
S	11.97	11.47	

Method of formation of the [illegible]

Kraus and McKee[1] did not isolate the asymmetrical product obtained with ammonia but from phenyl o-sulfo-

[1] loc. cit.

when the symmetrical chloride and phenol were heated at 40°-45° and this was the temperature employed in all following experiments.

2½ grams of the symmetrical chloride were mixed with 2 grams of phenol and heated for five hours at the temperature mentioned above. The mass was poured into water and washed with cold water and afterwards with boiling water. Most of the coloring matter was thus removed. After solidification it was finely triturated, filtered off, dried, and dissolved in glacial acetic acid, in which it was quite soluble. By fractional crystallization from this solvent there resulted which melted at 118°-119°, 103°-104°, and upon saponification was found to be the dibenzoyl ester of orthoamidobenzoic acid, the second orthoamidobenzoic

benzoate, and the third an unchanged portion of symmetrical chloride. The orthosulfobenzoic [illegible] but there was no evidence of the formation of phenyl orthosulfaminebenzoate.

Another portion of symmetrical chloride was heated with phenol as above and the product washed with cold water only. On crystallizing from glacial acetic acid, the same products were obtained as in the preceding experiment. Again, the reaction products were poured, without washing, directly into glacial acetic acid. After twelve hours a mass of crystals separated, but there was no evidence of the presence of any other substance besides those mentioned above. The crystals were filtered off and the filtrate poured into water. An oily substance separated which was extracted with ether, dried over calcium chloride, and allowed to stand. After some time a few crystals of

the diphenyl ester appeared, but nothing else was ever obtained. This part of the work was conducted very similar to the last ester prepared.

Showing that proof of the fact that neither ester contains the substance that produces phenyl orthosulphaminebenzoate on treatment with ammonia, the reaction products were poured into absolute ether and allowed to crystallize. The ether containing this solution was then put in a desiccator. Crystals formed slowly, and were removed from time to time and carefully examined. This was continued until the solution evaporated completely. No substances other than those already mentioned were discovered.

It became clear that the phenyl orthosulphaminebenzoate must have been formed by the action of ammonia upon the symmetrical chloride that remained when the ether [illegible]

action between the chloride and phenol was never complete with five hours heating at 100°-110°. Occasionally, when the mass was not frequently stirred during the heating, the unacted upon chloride was present in considerable quantity. It was possible that ammonia in the presence of phenol would react upon this to form phenyl orthosulphaminebenzoate. So the following experiment was undertaken.

2 grams of phenol were dissolved in 25 cc. of dilute ammonia, and to this 2½ grams of saccharin chloride were added. Reaction began immediately. The mixture was connected to a clock reflux and added to the bottom of the vessel, and the solution became quite warm. After cooling for some hours, the oil solidified. This was filtered off, dried, and crystallized from alcohol. A mass of fine needles separated out which, melted at 119° and appeared to be the desired ester of orthosulphaminebenzoic acid, and so proved to be when recrystallized

acid and titled to analysis, [illegible] separated somewhat, it yielded [illegible] crystals which, on purification, melted at 131°-132°, and were [illegible] identical to those obtained by former methods.

The analysis of the needles gave the following results:

I 0.[illegible] [illegible] [illegible] [illegible] [illegible]

II 0.1582 " " 0.3122 " " " 0.0631 " "

III 0.1917 " " 0.[illegible] " " " 0.0[illegible] " "

IV 0.3514 " " 0.2213 " $BaSO_4$.

Calculated for $C_6H_4(^{COOC_6H_5}_{SO_2OC_6H_5})_2$.

C	64.37	[illegible]	[illegible]	[illegible]
H	3.99	[illegible]	[illegible]	[illegible]
S	9.05	[illegible]		

The above reaction was [illegible] in various ways. The chloride was dissolved in [illegible] and dilute ammonia slowly added with stirring. In some cases the mixture was allowed to [illegible] in contact,

it was washed with tap water or with ice water. Although orthosulphaminebenzoate was always formed, but the best yield was obtained when the chloride was dissolved in phenol and ammonia added in a very slight excess. The following equation expresses the reaction:

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 3C_6H_5OH. + 3NH_3 = C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases} + C_6H_4\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases} + 2NH_4Cl.$$

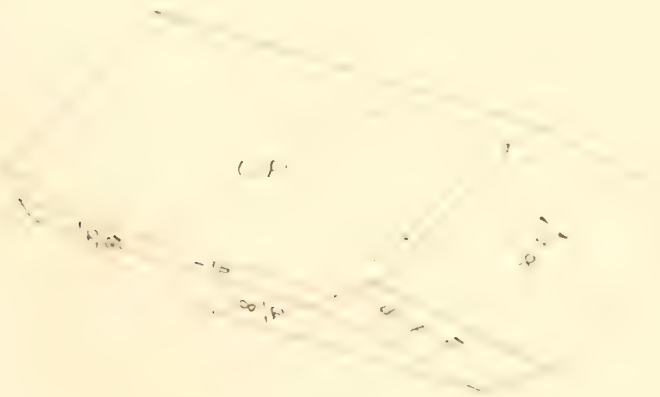
7 grams of meta-sulphonic chloride were treated as above with phenol and ammonia. The oily mass that first formed was stirred until it solidified. It was then filtered off and crystallized from alcohol. Needles of the dibenzoyl ester deposited. On water-ing of the filtrate from the needles, no other orthosulphaminebenzoate was obtained. The meta-sulphonic chloride could not be induced to yield this product, although the experiment was carried out under many conditions of temperature, and with variations of the sequence in mixing the materials.

The meta-nitrobenzal chloride is gradually poured into the ammonium salt of orthocyanbenzoic acid in alcohol, $C_6H_4(CN)SO_3NH_4$, and gently boiled until the odour of benzaldehyde ceases.

$$C_6H_4(CHCl_2)SO_3 + 2C_6H_5OH + 6NH_3 = C_6H_4(CN)SO_3NH_4 + C_6H_4(COOC_6H_5)SO_3C_6H_5 + 4NH_4Cl$$

Properties of Phenol orthocyanbenzaldehydesulphonate.

The melting point is 123°. It is easily soluble in alcohol, acetone, and glacial acetic acid; moderately soluble in benzene, etc., and distinctly soluble in ether, chloroform, water and petroleum benzine. The following illustrations show the crystal form.



[illegible] and flat prisms and, occasionally, left angular pyramids, [illegible] approximately 29° ; ab^c approximately 113°. γ was not determined. The basal cleavage is medium good, and the fracture vitreous. Medium index of refraction and low double refraction. Extinction + 5° 15' on the right prismatic face on basal section.

Action of Potassium Hydroxide.

1 gram of phenyl orthosulphaminebenzoate was heated in a beaker with an excess of dilute potassium hydroxide (10 cc. : 6 normal). In a few moments the entire quantity went into solution. This was allowed to cool. On the addition of concentrated hydrochloric acid there was an abundant precipitation of benzoic sulphimide. The filtrate had the odor of phenol when heated, and gave a precipitate of tribromphenol with bromine water. [illegible]

that the reaction proceeds according to the following equation:

$$C_6H_4\begin{matrix}COOC_6H_5\\SO_2NH_4\end{matrix} + 2KOH = C_6H_4\begin{matrix}CO\\SO_2\end{matrix}NK + C_6H_5OK + H_2O.$$

Action of Ammonia.

1 gram of phenyl orthosulphaminebenzoate was boiled with dilute ammonia. It went slowly into solution. When the reaction was complete, the solution was concentrated and strong hydrochloric acid added. Benzoic sulphimide was precipitated and the filtrate gave the test for phenol with bromine water. It has a slow but decided action upon the acid.

Action of Water.

1 gram of the ester was boiled with water in a flask connected with an inverted tube. In a short time it went completely into solution

[illegible] then recrystallized and the solution al-
[illegible]. A precipitate separated and was
[illegible] the melting point was 152° and the
substance proved to be the unchanged phenyl-
orthosulphaminebenzoate. The filtrate had a
slightly sweet taste. The filtrate and substance
were returned to the flask and heated for five
hours. On again cooling, crystals of phenyl ortho-
sulphaminebenzoate separated and the liquid was
somewhat sweeter than before. After 11 days boil-
ing the same thing occurred, but now the mother
[illegible]
precipitate of tribromphenol with bromine water.
Phenyl orthosulphaminebenzoate thus appears to be
decomposed by hot water, although with some diffi-
[illegible]
benzoic sulphinide and phenol. It is soluble in
hot water to an extent that permits of its
purification by this means.
[illegible]

of anthranilphenylglycocoll, the substance must be carefully washed, as it is readily soluble in hot water.

Action of Dilute Hydrochloric Acid.

1 gram of the substance was boiled with dilute hydrochloric acid in a flask connected with an inverted condenser. In a few minutes it went into solution. When the boiling was interrupted and the solution allowed to cool, the methanthranilphenylglycocoll crystallized out. The mother liquor gave no odor of phenol and no precipitate with bromine water. On continuing the boiling for an hour it was absorbed in the dilute solution [illegible] the residue extracted with a small amount of water. Barium carbonate was added to neutralization, the solution filtered and allowed

crystals of the neutral barium salt of orthosulphobenzoic acid crystallized out. They were in too small quantity to furnish an analysis, but there could be no mistake as to their character.

Phenyl Orthosulphaminebenzoate.

It seemed desirable to study the action of the cresols on the chloride of orthosulphobenzoic acid in order to see if it was analogous to that of phenol in the presence of ammonia. This was found to be the case. Only the ortho- and para-cresols were employed. They reacted with more difficulty than phenol and the yield was less than that of orthocresol. Both of the cresol orthosulphaminebenzoates were prepared from the unsymmetrical chloride. The unsymmetrical chloride used to [illegible]

[illegible] Orthosulphaminebenzoate

[illegible] symmetrical chloride was placed in a [illegible] with 1 gram of orthocresol and an excess of dilute ammonia. The whole is heated on a water-bath and vigorously stirred until the oily mass solidifies. This requires about ten minutes. The product must remain solid when heated up nearly to 100°. The symmetrical chloride is then converted into orthocresyl orthosulphaminebenzoate and the dicresyl ester of orthosulphobenzoic acid, the former largely predominating. It is purified by recrystallization from alcohol. The melting point is 152°. On cooling [illegible] the following [illegible] were obtained

I. [illegible] gram [illegible]

II. [illegible] 0.14-10 "

III. [illegible] [illegible] [illegible]).

IV. [illegible] 0.0195 " "

	Calculated for $C_6H_3 \begin{cases} NO_2 \\ SO_2NH_2 \end{cases}$.	Found.	
S	11.01	10.92	11.54
N	6.82	4.92	4.69

Paraoxysulphaminebenzoic acid.

This is made by the method mentioned above, employing paraoxysulphamine instead of the ortho variety. Paraoxysulphamine reacts more easily than orthoxysulphamine, and the formation of the dicarboxy. ester was much greater than in the preceding experiment.

It is impossible to say positively from a consideration of the foregoing reactions whether the amido-group is in the ~~carboxyl~~ sulphamic acid- or the sulphonic acid- groups, though they make it probable that it is the latter. In order to settle the question it would be necessary to study the action of [illegible] upon [illegible] sulphamine benzoic acid. Orthoxysulphaminebenzoic acid

$C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, and orthocarbaminesulphonic acid $C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}$ are both known, having been carefully investigated in this laboratory last year by Remsen and Wilson[1]. It was proposed to make the phenyl esters of each of these acids and condense them with the phenyl orthosulphaminebenzoate, so-called, and also by the action of phenol and ammonia on the asymmetrical chloride.

Phenyl Orthocarbaminesulphonate.

Orthocarbaminesulphonic acid was made according to the method given by Wilson. This was converted into the chloride by heating the ammonium salt with oxychloride of phosphorus. The chloride is placed in a beaker with a little more than the calculated quantity of phenol and a slight excess of dilute solution of potassium hydrate. The mixture is heated on a water-bath and stirred

[1] Dissertation 1899

the oily mass solidifies. It is then filtered off, carefully washed, and crystallized from alcohol. The crystals separate in the form of plates or needles; they are colorless, and the melting point is 96°. The products [illegible] above gave the following analytical results:

I. [illegible] gram [illegible] gram $BaSO_4$.

II. 0.1231 " " 0.1054 "

III. 0.2966 " " 0.0206 " N (Kjeldahl).

IV. 0.1095 " " 0.0216 "

Calculated for $C_6H_4\begin{cases}CONH_2\\SO_2OC_6H_5\end{cases}$ [illegible].

[illegible]	[illegible]	[illegible]
N	5.07	[illegible]

The method of formation clearly indicates that the correct formula of this substance is $C_6H_4\begin{cases}CONH_2\\[illegible]\end{cases}$. It is entirely different from the substance obtained from the asymmetrical chloride by treating with phenol and ammonia. Its melting point is 96° [illegible], and its mode of crystallization quite distinct.

Dissolved most of the reagents that easily salt upon phenyl orthosulphaminebenzoate it is stable. It resists the action of cold dilute potassium hydroxide. It is affected to a greater degree, and is not converted by it to a salt of benzoic sulphinide.

Phenyl Orthosulphaminebenzoate.

The attempt was next made to prepare the phenyl ester of orthosulphaminebenzoic acid, $C_6H_4(^{o}COOC_6H_5)(CO.NH_2)$. The acid was prepared according to directions given in [illegible] chloride of this acid, and an attempt was made to unsuccessful. Thinking the ester might be made by direct treatment of the acid with the acid, various methods were tried. The acid was warmed with phenol, and phosphorus oxychloride gradually added. A vigorous reaction resulted but no ester was formed. The acid was [illegible]

formed into benzoic sulphimide. When phosphorus pentachloride was employed instead of the oxychloride, the result was the same. When a mixture of the acid (1 part), phenol (2 parts) and concentrated sulphuric acid (1/10 part) was heated on the water bath for eight hours. At intervals of one hour, a small portion was removed and examined for the ester. It was found that the formation of benzoic sulphimide began immediately and continued slowly to complete reaction. No evidence of the formation of ester could be found. The ester, part of the acid was reduced and heated with phenol iodide at 120° for three days. As far as could be discovered, little or no reaction had occurred. Further efforts to prepare this ester were abandoned for want of time. While it was not possible to [illegible] it was clear that the [illegible] had been formed by treatment of the symmetrical chloride with phenol and ammonia, that the symmetrical

recently assigned the latter substance. Ethyl $C_6H_4(OH)(SO_3H)$ is rendered very probable by the fact that the phenyl ester of orthocresolsulphonic acid $C_6H_3(CH_3)(OH)(SO_3H)$ is quite of different substance. Other considerations leading to the correctness of this view will be taken up in the general discussion of results.

Orthocresolsulphochloride of Phenyl Benzoate.

This substance is formed from both chlorides by heating with phenol. In order to determine its properties relating to that of the diphenyl ester, formed at the same time, the following experiments were undertaken.

3½ grams of each chloride were placed in a test-tube with 2 grams of phenol and heated five hours in a sulphuric acid-bath. The various

of six experiments was made with each chloride, at each of the following temperatures: 40°-45°, 65°-70°, 100° and 135°.

At 40°-45°, the lowest temperature found practicable, the reaction proceeded very slowly, and was never complete with either chloride at the end of five hours. The red mass formed was poured into a mortar and rubbed with cold and hot water, until the colouring matter was removed as far as possible. This could not be completely effected, even by washing with dilute alkali. When poured into water, the reaction products form an oil which, as the washing proceeds, passes through a viscous stage to the solid state. This was then finely triturated, filtered off and dried. The product from the symmetrical chloride had a pale-yellow colour, and that from the unsymmetrical was nearly white. These were crystallized from glacial

[illegible] formed the disphenyl ester of orthosulfobenzoic acid and orthosulfochloride of phenyl benzoate, the former in much greater quantity. The disphenyl ester crystallizes in needles and orthosulfochloride of phenyl benzoate in heavy prisms. These could be roughly separated by the method of levigation, but only an approximate determination could be made of the relative quantities [illegible].

From the unsymmetrical chlorides, the orthosulfochloride of phenyl benzoate was formed almost [illegible], with a few crystals of the disphenyl ester [illegible].

After [illegible] the reaction products were [illegible] coloring matter. Some color remained even after most vigorous methods to remove it. When poured into a mortar and water added, each particle of

ones without passing through the ruby viscous stage. The crushed product from the asymmetrical chloride has a light-yellow color, while that from the unsymmetrical one was pink. The same products were formed as at the lower temperature, but in somewhat different proportions. [illegible] The same was found to be true in the case of the unsymmetrical [illegible] a very small quantity of anthracenchloranthracene is changed to anthracene and a relatively large quantity of dihydroanthracene. [illegible] were formed in nearly equal proportions.

At 130° the product from each chloride consisted wholly of dihydroanthracene.

Taking these facts into consideration, a good method of preparing anthracenchloranthracene and phenyl benzoate is as follows:

One molecule of magnesium oxide is heated with two molecules of phenol from twelve to thirteen hours at 120° ± 5°. The mass is thoroughly washed with hot water, allowed to crystallize, and recrystallized from glacial acetic acid. The crystals were large colorless prisms which melt at 104°-104.5° (uncorr.) recrystallized from alcohol they appear to be rhombic. It is easily soluble in alcohol and glacial acetic acid, difficultly soluble in ether and benzene. The substance investigated as above gave the following results on analysis:

I [illegible] gram gave 0.3600 gram CO_2 and 0.0611 gram H_2O.

II [illegible] " " 0.0666 "

III [illegible] " " 0.0520 "

IV. [illegible] " " [illegible] $BaSO_4$ 0.1954 "

V [illegible] " " [illegible]

	Calculated for $C_6H_4(COOC_6H_5)_2$		Found.	
I	72.62	5.56	72.99	[illegible]
II	3.06	3.63	3.29	[illegible]

Calculated for $C_6H_4(OH)_2SO_3Ba$		
	10.79	

Action of Acids, Water, Alkalies, etc.

Action of Hydrochloric Acid

In a small round bottomed flask connected with an inverted condenser, 2 grams of orthosulphonchlorobenzene were boiled with hydrochloric acid. The substance went completely into solution. This was evaporated to dryness on the water-bath and the residue dissolved in hot water. Some lime carbonate was added to neutralize the solution filtered and allowed to cool. Crystals of the neutral barium salt of orthosulphobenzoic acid were deposited. They were analyzed and gave the following results:

I. 0.1[illegible] gram gave [illegible] gram $BaSO_4$.

II. 0.1778 " " 0.1110 "

	Calculated for $C_7H_4SO_5Ba + 2H_2O$.	Found.	
Ba	36.79	36.93	36.75

$$C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + 2H_2O = C_6H_4\begin{cases}COOH\\SO_2OH\end{cases} + C_6H_5OH + HCl.$$

Action of Ammonia upon

The saponification with sulphuric acid was carried out just as with hydrochloric acid. After three hours the substance was completely converted to orthosulphobenzoic acid, phenol and hydrochloric acid. The neutral barium salt was made.

I. 0.1[illegible] gram gave [illegible] gram $BaSO_4$.

II. 0.1863 " " 0.1171 " "

	Calculated for $C_7H_4SO_5Ba + 2H_2O$.	Found.
Ba	[illegible]	[illegible]

Action of water.

Orthosulphonatobenzoate of phenyl benzoate was found to be saponified after boiling with water for six hours. The barium salt of the orthosulphobenzoic acid formed gave the following analytical results:

I. 0.1503 gram gave 0.0940 gram $BaSO_4$.

II. 0.1851 " " 0.1157 " "

	Calculated for $C_7H_4SO_5Ba + H_2O$.	Found.	
Ba	36.79	36.81	36.75

Action of Barium-Hydroxide.

The substance was boiled with a solution of barium hydroxide which was saturated at the ordinary temperature. After two hours the thick oily drops floating about in the liquid solidified in a crystalline condition, and much boiling produced no change. The solid was filtered off, washed, and crystallized from alcohol. Fine needles separated which melted at 115° and had the weli-

ferrous appearance of the diphenyl ester of orthosulfobenzoic acid. [illegible] barium orthosulfobenzoate.

I. 0.1875 gram gave 0.1171 gram $BaSO_4$.

II. 0.1946 " " 0.1210 " "

	Calculated for $C_{14}H_{10}SO_5Ba + 2H_2O$.	Found.	
Ba	36.79	36.96	36.59

The results gave the following analysis for carbon and hydrogen:

I. 0.1752 gram gave 0.4115 gram CO_2 and 0.0625 gram H_2O.

II. 0.1990 " " 0.4600 " " " 0.0704 "

	Calculated for $C_6H_4\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases}$.	Found.	
[illegible]	[illegible]	[illegible]	[illegible]
H	3.95	4.02	3.96

The formation of the diphenyl ester under these conditions was unexpected, although it is easily explained as a special form of the Schotten-Baumann reaction.

A similar experiment was carried out with the di-

into solution of potassium hydroxide. There was a gradual formation of the diphenyl ester which continued for two hours, when the reaction was complete. The [illegible] the [illegible] the [illegible] the precipitate was [illegible] the preceding experiment.

Action of Ammonia.

Ammonia has only a slight action on orthosulphonchloride of phenyl benzoate in the cold. But on raising the temperature the reaction proceeds vigorously and the production [illegible] a portion of the mixture was heated [illegible] with fresh [illegible] in a flask fitted with an inverted condenser. It went slowly into solution, and the reaction was complete after [illegible]. The solution was evaporated to small volume, filtered, and allowed to cool. On the

addition of strong hydrochloric acid, a substance was precipitated which proved to be benzoic acid. The solution was evaporated with ammoniacal water.

1 gram of the substance was dissolved in absolute ether and the solution placed in a small cylinder which was kept cool with ice water. Dry ammonia gas was slowly passed through this for an hour. A white precipitate gradually formed, and this was filtered off and dried. A portion of this was dissolved in water. With silver nitrate, there was formed a precipitate of silver chloride. Another portion dissolved in water gave a precipitate of benzoic sulphimide on addition of strong hydrochloric acid. Another portion yielded ammonia when heated with alkalis. The filtrate, when allowed to evaporate, yielded a few crystals of unreacted

orthosulphonchloride of phenyl benzoate, and an oily residue which had a strong odor of phenol.

The above experiment was repeated and the ether kept at a temperature of 30°. The reaction [illegible] Ortho-sulphonchloride of phenyl benzoate is decomposed [illegible] The following equation.

$$C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + 3NH_3 = C_6H_4\begin{cases}CO\\SO_2\end{cases}N.NH_4 + NH_4Cl + C_6H_5OH.$$

Action of Aniline.

It was thought that aniline would react with orthosulphonchloride of phenyl benzoate to form $C_6H_4\begin{cases}COOC_6H_5\\SO_2.NH.C_6H_5\end{cases}$ orthosulphonanilide of phenyl benzoate. [illegible] aniline to which an equal weight of this was added [illegible] of phenyl benzoate. The oily mass was formed which slowly solidified. The solid was [illegible]

from aniline, by washing first with dilute hydrochloric acid and finally with water, crystallizing from boiling acetic acid, and dissolving in chloride of phenyl benzoate first separated. There afterwards a small quantity of long, white, blades which melted at 190°-191°. They were insoluble in water and alkalies, and proved to be the anil, $C_6H_4\langle{}^{CO}_{SO_2}\rangle N.C_6H_5$, described by Remsen and Coates. When the substance is treated with pure aniline the yield of the anil is quite good. No evidence of the formation of orthosulphamine of phenyl benzoate was observed. Finally, the substance was dissolved in ether, and to this was added an ether solution of aniline. The reaction was very slow. Only the anil, in small quantity, was formed.

$$C_6H_4\langle{}^{CO.O.C_6H_5}_{SO_2Cl} + C_6H_5NH_2 = C_6H_4\langle{}^{CO}_{SO_2}\rangle N.C_6H_5 + C_6H_5OH + HCl$$

It appears, then, that the orthosulphonic anhydride can not be formed by such methods. The action

can not stop short with the removal of one hydrogen atom, as in uniting with the chlorine atom of o-nitrobenzenesulphonchloride of phenyl benzoate, but extends to the uniting with both these atoms of chlorine and oxygen.

Action of Benzene in presence of Aluminium Chloride.

The attempt was made to get the compound, $C_6H_4\begin{cases}CO.OC_6H_5\\SO_2C_6H_5\end{cases}$, by means of this reaction. It was supposed that such a substance could very probably be saponified to form the acid, $C_6H_4\begin{cases}COOH\\SO_2C_6H_5\end{cases}$, which is being investigated in this laboratory by Mr. Lowater. If such a transformation could have been brought about, it would have shed some light on the structure of [illegible]. Unfortunately, the reaction with Benzene could not take place, although the experiment was Tried in various ways. A precedent under [illegible] was encountered by Hollis[1] in treating the chloride

[illegible] 23, 242.

of paranitroorthosulphobenzoic acid with benzene in the presence of aluminium chloride. [illegible] were able to get the substance, $C_6H_4NO_2$ [illegible], but our attempts to prepare [illegible] times, as [illegible] were fruitless.

Action of Absolute Alcohol.

5 grams of the substance were placed in a small flask connected with an inverted condenser and boiled with absolute alcohol for fifteen hours. The alcohol was distilled off and the residue heated on the water-bath to expel the last traces of hydrochloric acid. This residue had a strong odor of phenol. A small quantity of water was added and the solution neutralized with barium carbonate. The filtrate from the excess of the carbonate was evaporated to a small volume and a few cubic centimeters

of alcohol and [illegible] separated out. These were filtered off, washed with alcohol and dried. Analysis gave the following results:

I. 0.3906 gram lost 0.0044 gram when heated to 150°.

II. 0.1035 gram gave 0.0500 gram $BaSO_4$.

III 0.3239 " " 0.1557 " "

IV 0.2439 " " 0.1171 " "

	Calculated for	Found.		
Ba	28.42	28.29	28.28	

Add a sentence to show that this needs further [illegible].

Action of Phenol.

When the [illegible] are heated with phenol, the formation of the diphenyl ester is greater the higher the temperature employed. At 150° it forms the sole product. It was found that by heating [illegible] prepared methylamine salts of phenyl urethane with phenol for five hours at 110°, it

was completely transformed into diphenyl ester

Action of Heat in presence of dilute Potassium Hydroxide.

(It was mentioned in a previous part of this paper, when the attempt is made to saponify o-chlorosulphonilchloride of phenyl benzoate with alkalis, the reaction is always accompanied by the formation of diphenyl ester, of o-chlorosulphobenzoic acid. This suggested the following experiments.

1 gram of orthosulphonechloride of phenyl benzoate was boiled with an excess of phenol and dilute potassium hydroxide. In a short time, the oily mass first formed solidified. It was filtered off and crystallized from alcohol. Needles of the diphenoxy ester separated, and this was the sole product. The reaction was smooth and rapid.

1 gram each of the symmetrical and unsymmetrical chlorides were treated with phenol and the smallest possible excess of dilute potassium hydroxide in the cold. The viscous masses first formed were stirred until they solidified. On crystallization from glacial acetic acid, it was found that nothing but diphenyl ether was formed from the symmetrical chloride; but both diphenyl ether and orthosulfobenzoic ~~acid~~ phenyl benzoate were formed from the unsymmetrical. [illegible] care is taken to keep the temperature low, the orthosulfobenzoic phenyl benzoate may be obtained in nearly pure condition by means of this reaction. It is a convenient and rapid method for preparing all the members of this class of compounds. [illegible] with phenol is employed, the process is long, and coloring matters are formed at the same time that

Action of the Cresols on the Chloride of Trichloracetophenonic Acid.

[illegible] chloride were heated with one gram of metacresol at 60°-65° for two days. This was the lowest temperature at which a speedy good reaction would take place. Even at this degree, two days heating were required to obtain a good result. Calomel mortar was formed in large quantity with such chloride, and was very hard to remove. The solid product was crystallised from glacial acetic acid. From the supernatant mother liquid white wool-like crystals were obtained. From the [illegible]

there was formed the [illegible] of the
above [illegible]. This crystallizes in rhombic tables
forms and melts at 115°. The substance was ana-
lyzed with the following results:

I. 0.2512 gram gave 0.1175 gram AgCl.

II. 0.2360 " " 0.1112 " "

III. [illegible]

[illegible]. Found.

Cl 11.41 11.15 11.64

[illegible] 10.1

When the chlorides are treated with ethereal
and dilute potassium hydroxide, the oxygenated
ring goes over easily into ethereal chloride of
orthocresol benzoate. The hydrochloric is decom-
posed by the alkali without the formation of thio-
substances or the disulphonated ethers in any con-
siderable extent. Only a few crystals of the
latter could be obtained. These had the form of

needles, separating somewhat the crystals of the
diphenyl ester. Melting point 101°. The difference
encountered in the formation of the ester must
be due to the retarding influence of the e
position. The diphenyl ester is formed with
the greatest ease by this method, since the
diphenacetyl ester is also obtained without
[illegible]

The orthonitrobenzenesulphonate of paracresol
is obtained by heating the unsymmetrical chlo-
ride with paracresol, or by treating it with
[illegible]
Same diphenacetyl ester is obtained at the
same time if the temperature is either too low
or too high. The unsymmetrical chloride under
[illegible]

The results and conclusions reached in this investigation may be summarized as follows.

1. The work of Remsen and McKee has been continued.

2. The method of formation of phenyl orthosulph aminobenzoate has been discovered. The reaction has been shown to be general, similar compounds having been obtained in the cases of the ortho and meta sulfamidobenzoic acids.

3. The structure of phenyl orthosulphaminobenzoate, discovered by Remsen and McKee, has been established beyond reasonable doubt. It is to be represented by the graphic formula $C_6H_4\begin{cases}O.CO.C_6H_5\\SO_2.NH_2\end{cases}$. The considerations in favor of this structure are: (a) the formation from the symmetrical chloride alone, showing that it probably has the symmetrical form; (b) it is quite a stable substance. From the phenyl ester of orthosulphaminobenzoic acid, $C_6H_4\begin{cases}O.CO.C_6H_5\\SO_2.NH_2\end{cases}$, it is easily transformed into benzoic sulphinide by

[illegible] (c) attempts to prepare [illegible] ortho-aminobenzoic acid [illegible] reaction goes too far and results in the formation of benzoic sulphinide; (e) the compounds of the acid have a great tendency to pass to benzoic sulphinide.

7. [illegible] the action of the methyl ester [illegible] on phenol in the presence of ammonia. The symmetrical chloride gives dibenzyl ester of orthosulphobenzoic acid and phenyl orthosulphaminobenzoate; while the unsymmetrical gives dibenzyl ester of orthosulphobenzoic acid, ammonium orthosulphaminobenzoate and a small quantity of benzoic sulphinide.

5. On heating the two chlorides with phenol, dibenzyl ester of orthosulphobenzoic acid and orthosulphonechloride, phenyl benzoate are form-

ed from each, the proportion [illegible] upon the temperature.

6. The method of formation and the reactions of o-benzenesulphonchloride of phenyl benzoate go to show pretty clearly that it has the structure represented by the formula, $C_6H_4 \begin{cases} COOC_6H_5 \\ SO_2Cl \end{cases}$. That it is symmetrical is shown by the fact that it easily goes over into dibenzoyl oxide when heated with phenol, or when treated with phenol and dilute alkali; also by the fact that it is [illegible] That it is a sulphonoxide is made probable by the fact that on treatment with ammonia it is transformed [illegible] o-benzosulphaminebenzoate, $C_6H_4 \begin{cases} COOC_6H_5 \\ SO_2NH_2 \end{cases}$, an intermediate product, which [illegible]

[illegible] and [illegible] of the
[illegible] both readily transformed
into [illegible] by the action of ammo-
nia, owing their similar structure

Biographical Sketch

The author was born in Washington County, Virginia April 1, 1862. His early education was received in private schools near Emory, Va. He entered Emory and Henry College (Virginia) in 1883, and received the degrees of Bachelor of Arts in 1889 and Master of Arts in 1892. During the last year in college he acted as Assistant in Greek. For two years he was Instructor in Mathematics in Hiwassee College, Tennessee. He was then appointed Instructor of Science in Centenary College, Tennessee, which position he held for five years.

In 1891 he was married to Miss Adelaide Summerfield Brunner, daughter of Dr. John H. Brunner, President of Hiwassee College.

In 1897 he entered the Johns Hopkins University as a student in chemistry, geology and mineralogy, and has pursued these studies for the past three years. In June, 1900, he was appointed to an Honorary Hopkins Scholarship.